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THE EFFECT OF THE ISOCYANATE TRIMERISATION CATALYST ON THE CHEMICAL COMPOSITION AND STRENGTH CHARACTERISTICS OF POLYURETHANE-POLYISOCYANATE FOAMS

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Abstract. Nowadays polyurethane-polyisocyanurate (PIR) foams are in a wide use as structural and thermal insulation materials. Isocyanate trimerisation catalysts for foams synthesis have low selectivity in terms of isocyanurate formation. As a consequence, a significant number of target (primary) and (secondary) chemical processes occur during the synthesis of PIR foams. We estimated the dependence of isocyanate group consumption for the formation of the main primary and secondary products on composition isocyanate index by methods based on the internal standard. Indeed, with an increase in the isocyanate index, the conversion of isocyanate to isocyanurate decreases significantly. The paper examines the influence of trimerisation catalyst type on chemical composition and strength characteristics of PIR foams. Hence, catalysts based on organic salts of alkali metals are more selective to the isocyanate trimerisation process than tertiary amines and derivatives of quaternary ammonium bases.

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Introduction

Nowadays, rigid polyurethane foams are widely used as thermal insulation materials in construction, manufacture of household appliances and refrigeration equipment, transportation of liquefied natural gas, pipe insulation, etc. [1-3]. However, these foams are applied as cryoisolation materials for the space industry [4-6].

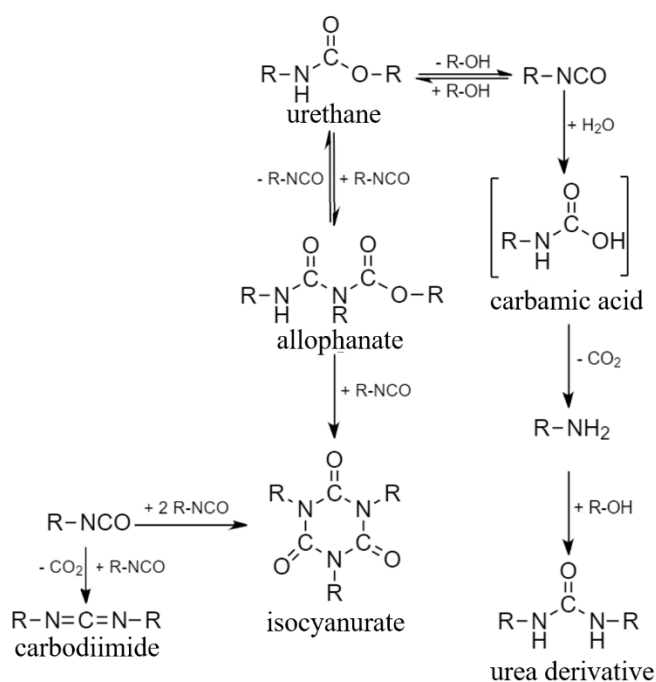
Moreover, efforts are being made to improve the strength characteristics, heat and fire resistance of polyurethane foams in regards to increasingly stringent requirements for construction foams. The first attempts to address this challenge began sixty years ago. It was realized in production of polyisocyanurate foams modified with urethane groups [7-10].



Chemically, urethane-modified macromolecules are copolymers, mainly consisting of chains of polyurethane and polyisocyanurate. However, the essential parameter used for the synthesis of such a polymer matrix is the so-called isocyanate index (II). It is determined by the excess of isocyanate over the theoretically necessary amount of substance for interaction with active hydrogen-containing groups capable of interacting with isocyanates.

To obtain isocyanate bonds in the compositions, appropriate catalysts are used to facilitate the process of isocyanate groups trimerisation. Therefore, this reaction kinetics and effective catalysts used in the production of isocyanurate-containing polymers were studied [11, 12].

The trimerisation of isocyanate groups can proceed spontaneously at a temperature of 373 K even in the absence of catalysts [13]. Process under milder conditions requires a wide range of additives. They are, in general, bases such as tertiary amines, quaternary ammonium bases, carboxylates, alcoholates, phosphites, phosphines and other derivatives of potassium, sodium, iron, cobalt, tin, etc. [14-18]. There are a lot of substances capable of catalysing the isocyanate trimerisation reaction. However, the selectivity of these substances in terms of the process is extremely low. As a consequence, the synthesis of polyurethane-polyisocyanurate foams involves the formation of target (primary) products as well as a number of side (secondary) bonds:



Depending on substance composition, the actual number of secondary chemical reactions may be significantly higher. A more detailed analysis isocyanate trimerisation mechanism into isocyanurate and description of side chemical processes are presented in [19-23].

Those secondary chemical processes can significantly effect on chemical composition and physico-mechanical properties of the obtained PIR foams. This problem is understudied. Therefore, to identify their effect on the strength characteristics of materials, we made a quantitative assessment of primary and secondary chemical processes in polyurethane-polyisocyanurate foams.



The experimental part

Initial reagents

Aromatic polyisocyanate by Voranate M229 brand (Dow, the Netherlands), mixture of simple polyester polyols, an organosilicon foam stabiliser (Evonik Ind., Germany), water, n-pentane (H.Ch., Ekos-1, Russia) as foaming agents were used as a composition for polyurethane-polyisocyanate foams production; pentamethyldiethylenetriamine (Evonik Ind., Germany), potassium acetate solution in diethylene glycol (in a mass ratio of 30:70, Evonik Ind., Germany) were used as catalysts. Polyisocyanate injected into the component was varied to achieve a given isocyanate index. PIR foams with isocyanate indices 150-400 in increments of 50 units were obtained. The amount of trimerisation catalyst (potassium acetate) introduced into the component was changed in a trend similar to that for polyisocyanate.

The choice of PIR foams formulation based on polyesters is a result of their infrared spectra. There are no intense absorption bands in areas that can be used in the study of reactions occurring during the synthesis and subsequent storage of the studied materials.

2,4,6-tris-(dimethylaminomethyl)phenol, 3-[3,5-bis[3-(dimethylamino) was used as alternative catalysts for trimerisationpropyl]-1,3,5-triazine-1-yl]-N,N-dimethylpropane-1-amine, 2-hydroxy-propyltrimethylammonium formate, 2-[(2-hydroxy-5-nonylphenyl)methylmethylamino]sodium acetate, 2-ethylhexanoate of 2-hydroxypropyltrimethylammonium, potassium acetate, 2,2-dimethylpropionate-N,N,N-trimethylmethanamine, and 2-ethylhexanoate of potassium (Evonik Ind., Germany). The additives were both pure substances and solutions in diethylene glycol and dipropylene glycol.

Phenylisocyanate (Acros Organics, Belgium) and 3-methyl-1-phenyl-2-phospholene-1-oxide (Alfa Aesar, USA) as catalysts were used for diphenylcarbodiimide synthesis. Phenylisocyanate was purified by distillation at reduced pressure.

All materials used were provided by OOO Izolan, Vladimir, Russia.

Foam synthesis methodology

To obtain samples of foams, mixed polyester component sample weights were placed in glass vessels with a volume of 1000 cm³; calculated amount of n-pentane was added; the mixture was intensively mixed for two minutes. Further, polyisocyanate was introduced into the system and the mixture was stirred for five seconds by an automatic mixer at 3000 rpm. Containers were tightly closed with a lid, preventing air contact with the forming foam. To completely exclude air penetration into the vessel, the joints of the lid and glass were coated with T-1 paraffin (Lukoil, Russia).

The second series of PIR foams with an isocyanate index of 350, obtained using various trimerisation catalysts, was synthesised similarly. However, foaming was performed in plastic cups with a volume of 1000 cm³ without additional insulation of the formed foam.

Methodology of infrared spectroscopic analysis

The IR spectra of the samples were recorded on a Perkin Elmer FT-IR Spectrum Two spectrometer equipped with a diamond prefix of attenuated total reflection (ATR). The spectra



were recorded in the area 4000-650 cm^{-1} at a temperature of 21 °C with a resolution of 4 cm^{-1} . For each spectrum ATR correction and an automatic baseline were performed.

We made the quantitative assessment of isocyanate groups consumption for formation of the main primary and secondary products contained in PIR foams by the method of the internal standard described in [24, 25].

Elemental analysis methodology

The elemental analysis of the synthesised diphenylcarbodiimide was performed as an additional indicator of synthesis results correctness. The analysis was performed on PerkinElmer Series II CHNS/O Analyser in accordance with the ASTM D5291-21 standard. The values of elements ratios for analysed substance were determined by the results of three independent measurements.

Apparent density determination methodology

The apparent density of the synthesised foams was determined in accordance with the ASTM D1622 standard; cubic samples of 50mm×50mm×50mm were cut from the obtained materials. The paper presents the average values obtained by results of five independent measurements.

Method of determining compressive strength

The compressive strength was determined in the direction of foaming on the Roell/Zwick Z005 universal testing machine at a deformation rate of 10 mm/min with 10% linear deformation in accordance with the EN 826:2013 method. Relative values of compressive strength are given, numerically equal to the ratio of compressive strength to the square of foam sample apparent density [26]. The result is an average value calculated by five independent measurements.

The main body

In [24], we proposed a method for quantifying the consumption of isocyanate groups for the main primary and secondary chemical processes occurring during the formation and storage of polyurethane-polyisocyanate (PIR) foams. This paper considers the reactions of allophanate and carbodiimide groups formation as the main secondary processes. One of the by-products (secondary) in the composition of PIR foams is carbodiimide. The active formation of carbodiimide bonds during the synthesis of pyrpenes occurs only at synthesis late stages at temperature about 150 ° C in forming polymer core [27]. The carbon dioxide released during the reaction sharply increases the volume of the foam. However, assessment of isocyanate consumption for carbodiimide groups formation is very interesting.

To quantify the content of carbodiimide groups in the analysed foams, we developed methodology based on the method of the internal standard. The calibration of the proposed quantitative assessment method was in accordance with the methods described in [24, 25]. The



synthesis of the model diphenylcarbodiimide was in accordance with the procedure by Campbell *et al.* [28]. The correctness of the synthesis was tested by IR spectroscopy and elemental analysis (see Table 1). The value of the calibration constant was 0.022 ± 0.001 .

Table 1. The results of synthesised diphenylcarbodiimide elemental analysis

Molecular formulae	
Theoretical	Experimental
$C_{13}H_{10}N_2$	$C_{13,1}H_{9,8}N_{2,0}$

The dependence of carbodiimide groups concentration on composition isocyanate index is shown in Fig. 1.

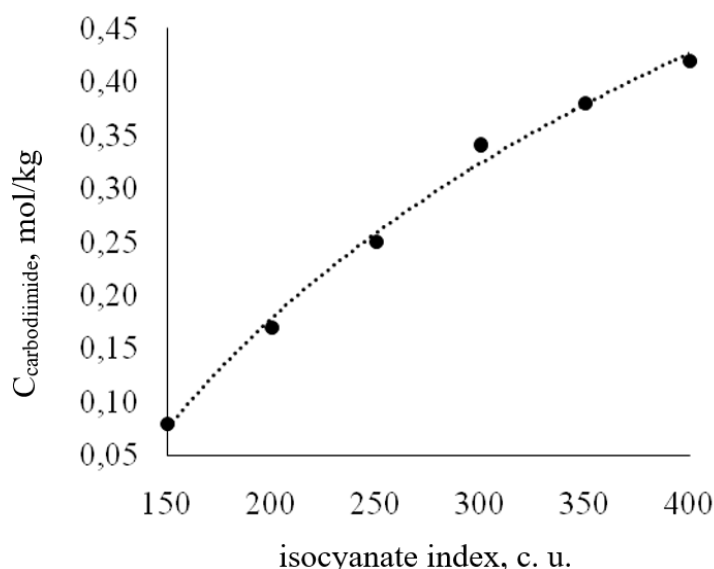


Fig. 1. The dependence of carbodiimide groups concentration on sample isocyanate index

Therefore, the amount of carbodiimide in PIR foam grows with an increase in the isocyanate index. It agrees with the results of Bhattacharjee *et al.* [29]. Rather sharp temperature decrease in active formation of carbodiimide bonds; their concentration remains unchanged.

However, to quantify isocyanate groups consumption for primary and secondary chemical processes we assumed the time of IR spectra registration is 10 minutes after mixing the components; all hydroxyl groups and water react with isocyanate to form urethane and a urea derivative (we will use the term urea hereafter). The correctness of this assumption is confirmed by the absence of analytical bands in the obtained IR spectra characteristic of hydroxyl groups valence vibrations.

The consumption of isocyanate groups for the formation of primary and secondary products, depending on composition isocyanate index is shown in Fig. 2. In accordance with the above assumption, amount of isocyanate spent on urethane and urea formation was estimated in terms of theoretical calculations; the amount of unreacted isocyanate groups and isocyanate for formation of allophanate, carbodiimide, and isocyanurate was calculated in accordance with the methods [24].

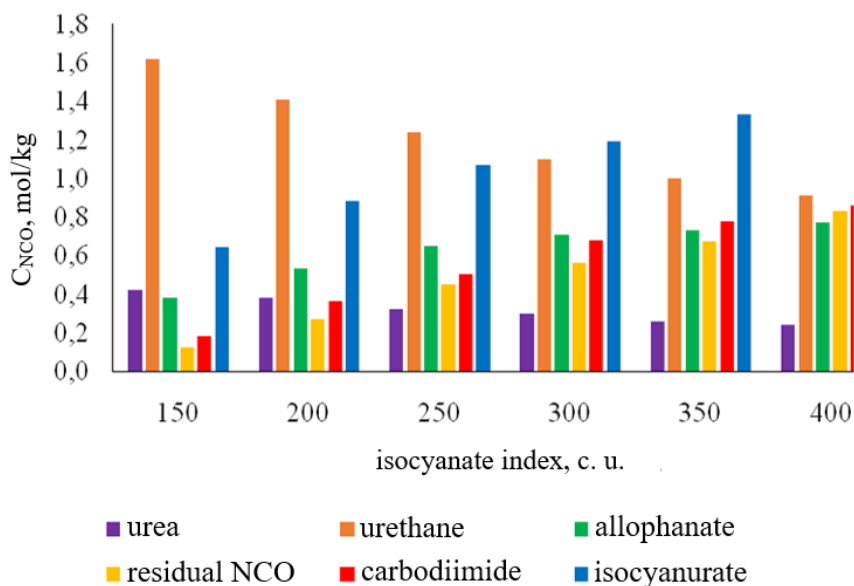


Fig. 2. Dependence of isocyanate groups concentration accumulated in the form of analytical groups on foam isocyanate index

By data in Fig. 2, the consumption of isocyanate for urethane and urea bonds formation decreases with an increase in the isocyanate index of the component due to a decrease in the mass fraction of the polyol composition in the initial mixture of components. Increasing in component isocyanate index causes higher consumption of isocyanate groups for the formation of allophanate, carbodiimide, and isocyanurate.

Indeed, an increase in the isocyanate index causes increasing of isocyanate spent on trimer formation. Nevertheless, it is important to assess the conversion of isocyanate groups. Those theoretically could enter the trimerisation process and convert to isocyanurate. The conversion of isocyanate to isocyanurate was calculated according to formula (1). However, calculation does not consider the isocyanate groups spent within the framework of the targeted (primary) chemical processes of urethane and urea bonds formation. Therefore, experiment considers only the concentrations of isocyanate groups that could potentially enter the trimerisation process. This dependence is shown in Fig. 3.

$$\text{Conversion} = \frac{C_{NCO \rightarrow \text{trimer}}}{C_{NCO \rightarrow \text{der. second. gr.}}} * 100 \quad (1)$$

where $C_{NCO \rightarrow \text{trimer}}$ is the number of isocyanate groups spent on isocyanate bonds formation; $C_{NCO \rightarrow \text{der. second. gr.}}$ is the number of isocyanate groups spent on allophanate and carbodiimide bonds formation and unreacted isocyanate groups.

According to Fig. 4, the conversion of isocyanate to isocyanurate decreases with an increase in the isocyanate index. Similar results were obtained in [30-32]. Indeed, the occurrence of secondary chemical processes (in particular, the accumulation of a significant number of isocyanate groups in the form of carbodiimide and allophanate) with an increase in the isocyanate index contributes to the emergence of significant spatial difficulties significantly complicating the process of trimerisation. However, with an increase in the isocyanate index, the amount of isocyanurate in the system increases (Fig. 2), the conversion of isocyanate to isocyanurate decreases significantly.



Table 2 shows the indicators of the apparent density and compressive strength of the obtained foams. The dependence of the relative compressive strength on the isocyanate index of the sample is shown in Fig. 4.

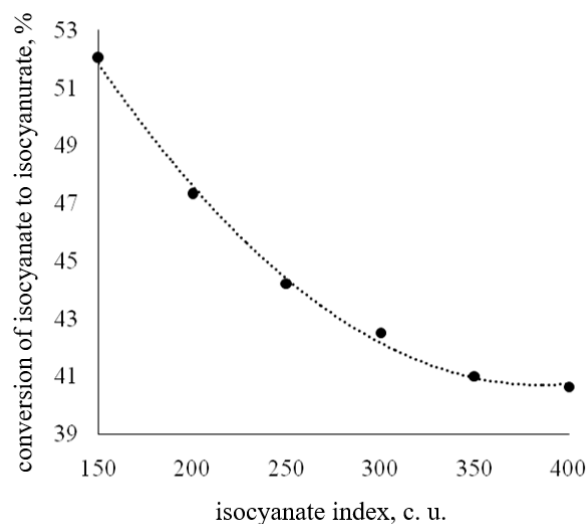


Fig. 3. Dependence of isocyanate groups conversion to isocyanurate on the isocyanate index of the sample

Table 2. The apparent density and compressive strength of the obtained PIR foams.

Isocyanate index	150	200	250	300	350	400
γ , kg/m ³	50.1	49.9	50.2	50.2	50.0	50.1
σ , kPa	188.4	223.8	277.5	314.6	349.7	378.3

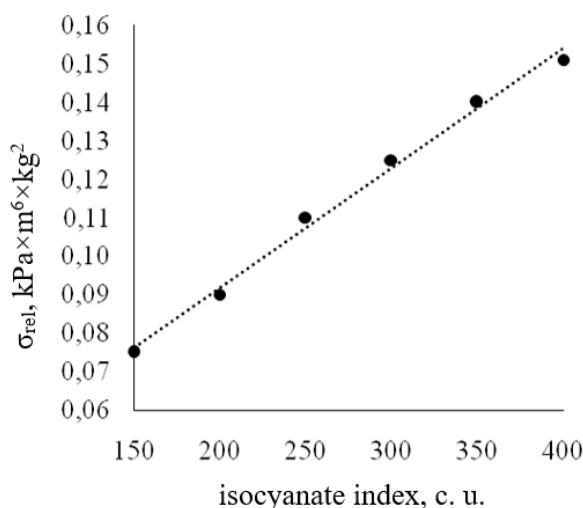


Fig. 4. Dependence of the relative compressive strength on the isocyanate index of the PIR foam

Dependence in Fig. 4 shows an increase in isocyanate index causes growing of the relative compressive strength index in terms of the range of isocyanate index values. It corresponds to the conclusions of Modesti *et al.* [30]. However, this effect is achieved mainly due to an increase in the concentration of three-functional isocyanurate groups. It contributes to growing of formed foam crosslinking degree. Although, the issue of secondary chemical processes depth influence on physical and mechanical characteristics of PIR foams remains undefined.



Moreover, in the analysed literature we were unable to find data on the influence of the side reaction products on the strength characteristics of polyurethane-polyisocyanurate foams.

As mentioned above, the chemical nature of the various isocyanate trimerisation catalysts used in the synthesis of PIR foams may vary significantly. Indeed, these additives are relatively weakly selective. As a result, the same catalyst can effect on primary and secondary chemical processes to differing degrees. In this case, there will be changes in both the chemical composition and the resulting changes in the physical and mechanical characteristics of the final product.

Therefore, to simultaneously study the effect of trimerisation catalysts on the secondary processes and the strength characteristics of foams, a series of PIR foams with an isocyanate index of 350 was obtained. We used 2,4,6-tris-(dimethylaminomethyl)phenol (I), 3-[3,5-bis[3-(dimethylamino)propyl]-1,3,5-triazin-1-yl]-N,N-dimethylpropan-1-amine (II), 2-hydroxy-propyltrimethylammonium formate (III), 2-[(2-hydroxy-5-nonylphenyl)methylmethylamino]sodium acetate (IV), 2-ethylhexanoate 2-hydroxypropyltrimethylammonium (V), potassium acetate (VI), 2,2-dimethylpropionate-N,N,N-trimethylmethanamine (VII) and potassium 2-ethylhexanoate (VIII) as catalysts. The list of catalysts under consideration contains tertiary amines, carboxylates of quaternary ammonium bases, and alkali metals.

These trimerisation catalysts were introduced into the component used for the synthesis of foam in equimolar amounts (0.01 mol of the active substance) both in the form of pure substances and as solutions in diethylene glycol or dipropylene glycol. The hydroxyl number of the final polyol compositions was equated by introducing a predetermined amount of diethylene glycol, if necessary.

Using the methods described above, the concentrations of unreacted isocyanate groups and the groups spent on the formation of isocyanurate, carbodiimide and allophanate were estimated in the analysed samples after specified time intervals. The determined concentration values of these values are presented in Table 3.

Table 3. Concentrations of isocyanate groups spent on analytical groups formation in samples of PIR foams

Exposure time, h.	Catalyst							
	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
	$C_{\text{residualNCO}}$, mol/kg							
0.2	1.32	1.11	0.80	0.51	0.77	0.61	0.61	0.67
24.0	0.62	0.45	0.45	0.38	0.39	0.42	0.35	0.24
	$C_{\text{NCO} \rightarrow \text{carbodiimides}}$, mol/kg							
0.2	0.40	0.40	0.58	0.60	0.68	0.76	0.70	0.78
24.0	0.40	0.40	0.58	0.60	0.68	0.76	0.70	0.78
	$C_{\text{NCO} \rightarrow \text{isocyanurates}}$, mol/kg							
0.2	0.52	0.73	1.04	1.01	1.09	1.27	1.19	1.34
24.0	0.54	0.76	1.07	1.05	1.13	1.31	1.23	1.38
	$C_{\text{NCO} \rightarrow \text{allophanate}}$, mol/kg							
0.2	0.89	0.76	0.69	0.68	0.74	0.65	0.67	0.58
24.0	0.87	0.73	0.65	0.65	0.70	0.63	0.64	0.56

Therefore, during the curing of foams, the concentration of isocyanate spent on carbon diimide bonds formation was expected to remain unchanged; the proportion of groups



transformed into the isocyanurate form gradually increased. Isocyanate accumulated in an unreacted state and in the form of allophanate bonds was gradually consumed during the analysed time. To a certain extent, this consumption is due to the formation of new isocyanurate bonds. Indeed, the most of these groups interacted with air moisture with the subsequent formation of urea bonds.

Table 4 shows the dependence of compressive strength and column height of PIR foam on the type of used catalyst.

Table 4. Dependence of PIR foam properties on the type of trimerisation catalyst

Catalyst	h, cm	γ , kg/m ³	σ , kPa	$\sigma_{rel.}$, kPa \times m ⁶ /kg ²
I	97.0	63.7	394.2	0.097
II	128.3	54.8	347.6	0.116
III	129.6	45.0	266.8	0.132
IV	130.8	50.8	354.0	0.137
V	137.6	48.3	318.6	0.137
VI	143.8	48.2	324.9	0.140
VII	130.9	45.9	307.8	0.146
VIII	131.5	46.3	337.4	0.157

However, the apparent density, rise height of the obtained foams, and their compressive strength change significantly during the transition from one trimerisation catalyst to another. Apparently, the observed difference is a consequence of essentially different catalytic activity of the analysed substances in terms of proceeding chemical processes.

Hence, by comparing the values of strength characteristics of the obtained foams (Table 4) and concentrations of the considered groups (Table 3), the dependences of change in the foam strength characteristics on their chemical composition were plotted (Fig. 5).

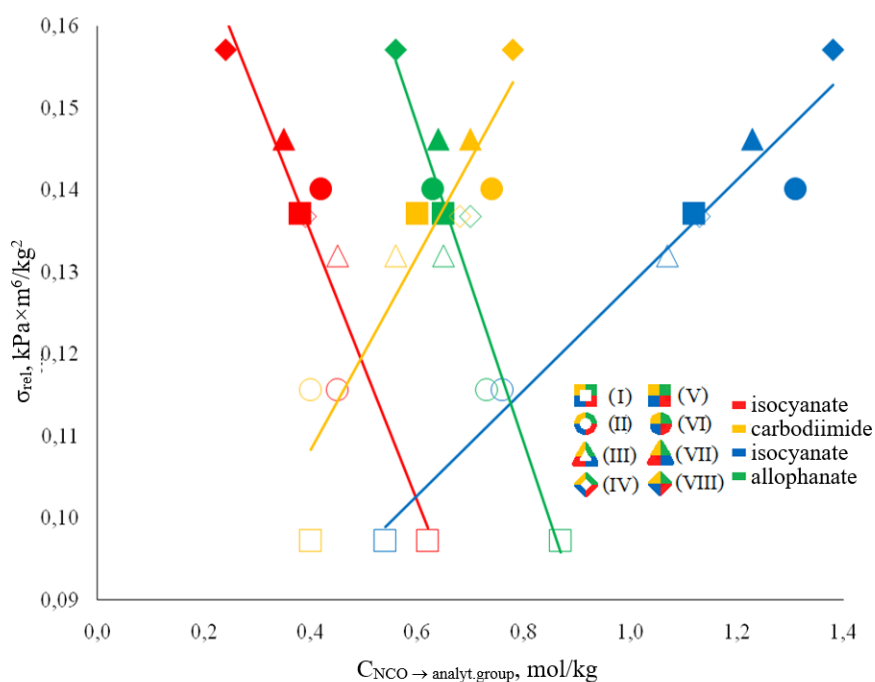


Fig. 5. Dependences of change in strength characteristics on chemical composition of PIR foams 24 hours after components mixing



Based on the data presented in Fig. 5, patterns of chemical composition influence on foam strength characteristics are observed. The relative compressive strength of the foam increases with an increase in the degree of isocyanate and carbodiimide crosslinking; this parameter decreases with an increase of free isocyanate and unstable allophanate bonds. These conclusions are partially consistent with the results of Modesti *et al.* [30]. In accordance to it, an increase of isocyanurate in the foam causes its strength characteristics improvement. However, increased isocyanurate causes foam fragility observing for pure polyisocyanurate foams. Therefore, it is necessary to maintain a balance of urethane, isocyanurate, and basic secondary groups in the composition to ensure it optimal strength characteristics.

In accordance with formula (1), the conversion values of isocyanate to isocyanurate were calculated for the analyzed samples. The data are presented in Table 5.

Table 3. Conversion of isocyanate to isocyanurate with the considered trimerization catalysts

Catalyst	I	II	III	IV	V	VI	VII	VIII
Conversion rate, %	22.2	32.5	38.9	39.2	39.0	42.0	42.1	48.3

Hence, the most effective in terms of catalysis of the trimerisation process are organic salts of alkali metals and quaternary ammonium bases. It agrees with the conclusion of Jianping *et al.* [33]. The most appropriate catalyst contributed to an increase in the conversion of isocyanate to isocyanurate were potassium 2-ethylhexanoate, potassium acetate, and 2,2-dimethylpropionate-N,N,N,-trimethylmethanamine, respectively. It corresponds to the conclusions made by Lovenich *et al.* [32]. Therefore, catalysts based on alkali metal salts made the trimerisation process more effective than salts of quaternary ammonium bases. It corresponds to the results of Dick *et al.* [34] and Clift *et al.* [35].

Conclusions and recommendations

The research proposes a technique for the quantitative analysis of isocyanate groups spent in the synthesis of PIR foams on the formation of isocyanate, allophanate and carbodiimide groups. With increasing isocyanate index of PIR foams the maximum possible conversion of isocyanate into isocyanurate decreases due to very active occurrence of hindering secondary chemical processes. The influence of various isocyanate trimerisation catalysts on the strength characteristics of the obtained foams and the completeness of the formation of isocyanurate, allophanate and carbodiimide is analysed. The compressive strength of PIR foams grows with increasing degree of isocyanurate and carbodiimide cross-linking and decreases with increasing content of allophanate and residual isocyanate groups. Hence, the highest conversion of isocyanate to isocyanurate can be achieved using 2,2-dimethylpropionate-N,N,N,-trimethylmethanamine, acetate and 2-ethylhexanoate of potassium as a catalyst for isocyanate trimerisation.

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